

PATENT SPECIFICATION

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(54) DENTAL RESTORATIVE COMPOSITE

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 ING AND MANUFACTURING COM-
 PANY, a corporation organized and existing
 under the laws of the State of Delaware,
 United States of America, of 3M Center,
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 of America, do hereby declare the invention
 for which we pray that a patent may be
 granted to us, and the method by which it is
 to be performed, to be particularly
 described in and by the following
 statement:—

This invention relates to dental
 restorative materials and, more particularly,
 to dental restorative compositions
 comprising a blend of polymerizable binder
 and particulate filler.

Composites useful as dental restorative
 materials comprising liquid organic
 polymerizable binder and finely divided
 inorganic solid filler are well known. See,
 for example, the compositions as described
 in U.S. Patent No. 3,066,112 (Bowen). As
 disclosed by Bowen, dental restorative
 composites comprising 17 to 34% by weight
 of a thermosetting resin such as the glycidyl
 methacrylate derivative of Bisphenol A,
 commonly referred to as BisGMA, and 66
 to 83% by weight of a filler (such as clear,
 colorless, fused silica having a particle size
 fine enough to pass through a number 325
 sieve of the U.S. Standard Sieve Series (44
 microns)) are acceptable as filling materials
 for restorative dentistry (having
 compressive strengths up to 23,000 p.s.i.).

These dental restorative composites by
 definition should restore both the function
 and appearance of a defective tooth and,
 consequently, a number of practical
 restrictions are placed upon a suitable
 material. The organic polymerizable binder
 employed in such composites must possess
 the property of rapid and complete
 polymerization under the conditions of the
 oral environment. The restorative material
 must exhibit low polymerization shrinkage,
 low water absorption, low solubility in the
 aqueous fluids of the mouth, low toxicity
 and satisfactory strength characteristics.
 Since these requirements cannot be met in

entirety by the resin itself, restorative
 materials are normally composites, that is,
 reinforcing filler materials are added to the
 resin to produce a composite having the
 desirable properties.

Addition of fillers to the liquid organic
 binder produces a restorative composite
 which, upon polymerization, hopefully
 compares favorably with the natural tooth
 crown in dimensional stability, abrasion-
 resistance, color, translucency and in
 strength so that the material will maintain its
 integrity and support the remaining tooth
 structure during mastication. The
 translucency of a polymerized dental
 restorative composite must compare to the
 natural translucency of the tooth. This
 requirement of a restorative composite is
 essential for aesthetically pleasing
 restoratives, particularly in the anterior
 portion of the mouth where composites are
 principally used. A polymerized composite
 restorative that is too translucent will
 appear as a glassy window-like portion
 within the tooth and, conversely, a
 composite restorative that does not have
 adequate translucency or is too opaque will
 appear as an opaque white spot on the
 tooth. Consequently, if the restorative
 material fails to meet these basic
 requirements it is not acceptable because it
 fails to restore or simulate the natural
 appearance of the tooth.

The basic physical and optical properties
 of the organic binder referred to in U.S.
 Patent No. 3,066,112 are adequate to
 produce a composite which possesses
 proper translucency for a natural-appearing
 restorative. The filler used must have an
 index of refraction which matches the index
 of refraction of the polymerized binder such
 that the translucency of the restorative
 composite matches that of the natural tooth
 structure. This property of translucency is
 tested by A.D.A. Spec. No. 9 for Dental
 Silicate Cement and should provide for an
 opacity by this test of about 35% (Co. 70).

Thus, most of the commercially available
 dental restorative composites are based
 upon the organic binder system referred to

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in the above-mentioned Bowen patent and most of these typically use quartz particulate fillers. The polymers have a refractive index of 1.50 to 1.55, and the quartz fillers also have refractive indices of about 1.50 to 1.55. According to some literature there should be a slight difference between the refractive indices of the resin and the filler for best appearance (i.e. a difference of about 0.005, but preferably not greater than 0.025).

However, recently there has been much desired for dental restorative materials having much improved compressive strength. Generally speaking, it is possible to increase the compressive strength by increasing the amount of particulate filler present in the compositions. And, consequently, in order to obtain high loadings of filler it is necessary for the filler to be in finely reduced state.

There are a number of patents which teach the use of a finely divided particulate filler in those restorative compositions. See, for example, U.S. Patents 3,709,866; 3,452,437; 3,629,187; 3,539,533; and 3,751,399. U.S. Patent 3,792,531 (Rossi) teaches a restorative composition in which finely divided particulate filler has a particle size of 0.7 to 30 microns, with care being taken to eliminate the presence of any appreciable amount of particles having a diameter less than 0.7 micron (since such particles are said to adversely affect the translucency of the restorative). German Offenlegungsschrift 2,403,211 describes a dental composition in which all of the finely divided filler is less than 0.7 micron in diameter (and preferably is much smaller). German Offenlegungsschrift 2,405,578 describes a dental composition in which the filler has a maximum particle size of 0.07 micron. Although mention is made that finely particulate glass (particle size less than 5 microns) may be present, it is present in amounts only up to 25% by weight of the total filler.

Contrary to the prior art, it has been found in the present invention that a significant increase in compressive strength is obtained, without sacrifice of desirable translucency, by using as the finely divided particulate filler a material having a particle size distribution such that a significant portion of the filler is in the range of 0.2 to 0.7 micron while the balance of the filler is in the range of 0.7 to 25 microns in size.

In accordance with the invention there is provided an improved dental restorative material prepared by mixing and polymerizing a liquid organic polymerizable binder and a finely divided particulate filler, the filler having a particle size distribution such that 70 to 95% by weight of said particles are in the range of 0.7 to 25 microns and correspondingly 5 to 30% by

weight of said particles are in the range of 0.2 to 0.7 micron in diameter.

The dental restorative materials of the invention exhibit excellent compressive strength and desirable translucency as compared to dental restorative materials having particulate filler of different particle size distributions.

Since the advantages obtained by the present invention are attributable to the particle size distribution of the particulate filler used herein, any liquid organic polymerizable binder may be used in this invention. There are a variety of known useful polymerizable binders. For example, the BISGMA type described in U.S. 3,066,112 are quite useful and are presently preferred in this invention. Such polymerizable binders preferable contain an amount of a reactive diluent (such as triethyleneglycol dimethacrylate or tetraethyleneglycol dimethacrylate) for purposes of reducing the viscosity thereof. The amount of diluent typically used for viscosity control is in the range of about 25 to 50% by weight of the polymerizable binder. Liquid polymerizable binders are also described in U.S. 3,539,533. Still another type of useful polymerizable binder is the photopolymerizable type described in U.S. 3,709,866. Other useful polymerizable binders are well known in the art.

The finely divided particulate filler which is useful in the practice of this invention must have a particle size distribution such that 70 to 95% by weight of the particles are in the range of 0.7 to 25 microns in diameter and correspondingly 5 to 30% by weight of the particles are in the range of 0.2 to 0.7 micron. Particles greater than 25 microns in diameter are not desired because when they are present in more than trace amounts they impart a greater surface roughness than desired, and they also tend to decrease the compressive strength of the restorative material. Although particles less than 0.2 micron in diameter may be used in the dental restorative as a conventional thickener, such particles should not be used in amounts exceeding about five percent by weight of the filler because, in addition to greatly increasing the viscosity of the binder prior to cure, they cause a decrease in the amount of filler which may be present with attendant decrease in compressive strength obtained after curing of the binder.

With particle size distribution used in this invention the median particle size is in the range of 1 to 5 microns and is accordingly smaller than that used in commercially available dental restoratives. Although others have heretofore suggested that large amounts of ultrafine particles (e.g. silica particles such as those available under the registered Trade Mark "Cab-O-Sil") may be

included in dental restoratives in addition to relatively large particles (e.g. 1 to 30 microns), the presence of a significant amount of ultrafine particles also significantly increases the viscosity of the liquid polymerizable binder. Consequently, it is not possible to incorporate a very high loading of filler into such restorative materials. As a result, such restorative materials do not exhibit high compressive strengths.

Surprisingly, however, it has been found that with the broad particle size distribution used in the present invention, and resulting small median particle size, it is possible to incorporate large amounts of particulate filler into dental restorative materials of the invention with correspondingly high compressive strength being obtained. Thus, in accordance with the present invention particulate filler may comprise 75 to 90% by weight of the restorative material. This is surprising in view of the fact that fine particles are expected to greatly thicken the liquid polymerizable binder and accordingly limit the amount of particulate filler which may be incorporated into the restorative. It is also surprising that the dental restorative materials of the invention exhibit desirable translucency since it would be expected that the presence of a significant amount of particulate filler having a diameter corresponding to the wavelength of visible light (about 0.7 micron) would impart significant opacity.

The types of finely divided particulate filler which may be used herein encompass those which are conventionally available and preferably have a Moh's hardness of about 3 to 8, more preferably 5 to 7. Thus, useful materials include crystalline quartz (so-called alpha quartz) which is presently preferred, fused silica, ground glass, synthetic siliceous materials, aluminum oxide, and other fillers which are well known in the art.

In order to achieve a dental restorative material having the proper translucency (i.e. 0.2 to 0.5 optical density units as measured by transmission densitometer), it is necessary for the refractive index of the particulate filler to closely match the refractive index of the cured binder resin, as is known in the art.

Although the conventional technique for preparing finely divided particulate filler is to grind relatively large particles in a mill jar until the desired particle size is obtained, it has been found that such technique is not totally satisfactory when using conventional grinding apparatus to prepare small particles such as those made of quartz. A conventional mill jar is made of ceramic and accordingly has a high alumina content (e.g. 70-80% alumina). Conventional grinding

media, used in the mill jar, such as porcelain balls and borundum also have a high alumina content. Flint pebbles, which are commonly used as grinding media, are made of silicon dioxide and further contain trace contaminants. Consequently, during normal milling the particles being prepared are unavoidably contaminated with alumina, or other contaminant, having a relatively high index of refraction.

Although this contamination does not significantly modify the refractive index of those particles which are about one micron or larger in diameter, the refractive index of particles which are about 0.7 micron in diameter (approximately the same as the wavelength of visible light) is drastically modified. Consequently, small particles which are prepared by conventional ball milling will be very undesirable for use in dental restoratives since their refractive index will differ from that of the larger particles (i.e. particles greater than about one micron in diameter) of the same material.

To overcome this inherent drawback associated with conventional ball milling techniques, the present invention provides an improved technique whereby very small particles of materials such as quartz may be prepared which are not undesirably altered in their refractive index. The improved technique may be referred to as autogenous milling, i.e. the grinding media has the same chemical makeup as the material to be ground into small particles. Further, the interior of the mill jar is lined with a tough, durable organic coating (e.g. polyurethane) which is preferably free of pigments and other inorganic contaminants. The grinding is done in the dry state because wet grinding of the particles results in a particle size distribution which is narrower than required in this invention. After the grinding is completed the particles are heated to a high temperature to remove any possible organic contamination thereof.

Thus, for example, in order to prepare quartz particles having the desired particle size distribution, quartz crystals (approximately 0.5 to 5 cm.) are used as the grinding media, and fractured quartz frit is used as the feed material. These materials are placed in the mill (preferably a vibratory mill having its interior lined as described above) and milling is continued in the dry state for several hours, after which the finely divided particulate quartz is recovered and heated to a high temperature (e.g. 900°C.).

The finely divided particulate filler to be used in the restorative should preferably be treated with a keying agent to improve the bonding between the filler and the bonding resin and also to reduce the moisture susceptibility of the filler-resin interface.

There are a variety of well known keying agents which are useful for this purpose. Preferred keying agents are the ethylenically mill having its interior lined as described unsaturated organosilanes. See, for example, the keying agents and technique described in U.S. 3,066,112 (Bowen). Other suitable keying agents are described in U.S. 3,539,533. Particularly preferred keying agents for use in this invention include gamma - methacryloxypropyltrimethoxy silane and vinyltrimethoxy silane. Other useful keying agents are well known in the art.

One manner for treating the finely divided particulate filler with a keying agent is described in U.S. 3,862,920 wherein gamma - methacryloxypropyltrimethoxy silane is dissolved in a water/acetone blend. The particulate filler is then mixed with the silane solution to form a slurry. The water and acetone are then removed at 100°C. after which the treated filler is heated at 125°C. for two hours. Another technique for treating the particulate filler with a keying agent involves dissolving the silane in toluene (e.g. to form a 50% solution) and then mixing the solution with the particulate filler, followed by drying the damp cake at 115°C.

The composite dental restorative materials of the invention are typically provided as two-part systems. Preferably the polymerizable binder is separated into two equal or approximately equal volume portions and the desired particulate filler is also separated into two portions and then admixed with the binder portions to form two pastes. The catalyst for the polymerizable binder is contained in one paste portion and an activator is contained in the other paste portion. Thus, the two pastes are each quite stable and may be separately packaged. Then, at the time of use, equal volumes of the pastes are mixed together thoroughly and placed in the tooth cavity to be filled. Curing of the binder then occurs in situ to provide a dental restorative having high compressive strength and desirable translucency.

The invention is further illustrated by means of the following non-limiting examples wherein the term "parts" refers to parts by weight unless otherwise indicated.

Example 1

Raw alpha-quartz is heated to 1000°C. and is then quenched by allowing the heated quartz to fall into water. The resulting fractured frit is dried at 150°C. and then cooled. This fractured frit is then charged into a lined vibratory grinding mill with quartz pebbles (0.5—5 cm. diameter) as the grinding media. The grinding mill itself is commercially available from Sweco, Inc. as

Model "DM-3". Before use the interior surface of the mill is lined with a tough polyurethane polymer ("Adiprene L-167", commercially available from E. I. DuPont, and cured with MOCA).

The fractured frit is milled for 48 hours to reduce the particle size. The resultant powdered quartz is then heated to 900°C. to remove organic contaminants.

After the finely divided filler is allowed to cool, it is passed through a 325 mesh nylon screen material. The resultant powdered quartz has the following distribution of particle sizes:

Particle Diameter (Microns)	Percent By Weight Finer Than
21	100
8.8	90
5.4	75
2.5	50
1.7	40
0.9	25
0.7	20
0.5	15
0.2	2

Example 2

An amount of the quartz particles prepared in accordance with the procedure of Example 1 are charged to a conventional powder blender along with four percent by weight (based on the weight of the quartz particles) of colloidal silica thickener ("Cab-O-Sill M-5", commercially available from Cabot Corporation). These materials are thoroughly blended after which eight percent by weight (based on the total weight of quartz particles and colloidal silica) of a 50% solution of gamma-methacryloxypropyltrimethoxy silane in toluene is added with further blending. After through blending the resulting damp cake is spread in thin layers, dried at 115°C. for one hour and then cooled.

Example 3

A two part paste dental restorative is prepared as follows:

A resin binder (containing an activator therefor) is compounded by adding 2.5 grams of N,N - di - (2 - hydroxyethyl) - p - toluidine to 48.8 grams of triethylene glycol dimethacrylate, followed by mixing until a solution is obtained. The solution is then thoroughly mixed with 46.5 grams of BisGMA (i.e. the glycidyl methacrylate derivative of Bisphenol A). Then 525 grams of the treated particulate filler prepared in Example 2 is added slowly with stirring until a uniform paste is obtained.

A resin binder (containing a catalyst) is compounded by dissolving 1.1 grams of benzoyl peroxide in 48.7 grams of triethylene glycol dimethacrylate. The resulting solution is then thoroughly mixed

with 49.3 grams of BisGMA. A small amount of a polymerization inhibitor (such as a substituted phenol) is also added. Then 525 grams of the treated particulate filler prepared in Example 2 is added slowly with stirring until a uniform paste is obtained.

Example 4

A tooth cavity is restored by first mixing equal volume portions of the two pastes prepared in Example 3. Typically the mixing is effected with a small spatula of wood, plastic or porcelain and requires only about 20 seconds. Then the restorative material is placed in the tooth cavity where the binder polymerizes in situ (in about two minutes) to form a dental restorative having high compressive strength.

Another sample of the cured dental restorative is immersed in water (37°C.) for 24 hours and then tested for compressive strength. A value of 55,000 p.s.i. is observed.

Example 5

A test sample of the dental restorative is prepared as follows:

Equal volume portions of the two pastes of Example 3 are thoroughly mixed and immediately placed in a ring mold (20 mm. in diameter) sitting on a polyester film (250 microns thick). The top of the ring mold is then covered with another piece of polyester film (250 microns thick), after which the entire mold assembly is placed in a press. The assembly is then subjected to a pressure greater than 20,000 p.s.i. in one second or less and such pressure is continued for at least five minutes. The pressure is then released and the test disk is removed from the mold. The steps of mixing the pastes, placing the mixture in the mold, and subjecting it to a pressure greater than 20,000 p.s.i. must be accomplished in one minute or less.

Example 6

The test disk prepared in Example 5 is placed on the stage of a conventional transmission densitometer (Macbeth Model "TD 501") which has been fitted with a light filter in the visible light region (calibrated to zero reading and also calibrated to the opacity range of dental restorative materials).

A measurement of the opacity of the test disk yields a reading of 0.25 optical density units (which means that the dental restorative has acceptable translucency).

Example 7

Raw alpha quartz is heated to 1000°C. and quenched by allowing the heated quartz to fall into water. The resulting fractured frit is charged into a lined vibratory grinding mill with quartz crystals as grinding media.

An amount of water equal to the weight of the fractured frit is also charged into the mill. The fractured frit is then milled for 26.5 hours. The resulting slurry was drained from the mill, dried in a forced air oven, heated to 900°C., and then screened through a 325 mesh nylon screen material. The resulting powdered quartz had the following particle size distribution:

Particle Diameter (Microns)	Percent by Weight Finer Than
11	100
7.4	90
5.2	75
3.4	50
2.8	40
2.0	25
1.6	20
1.1	10
0.8	5
0.7	2

The ground quartz is blended with colloidal silica and treated with the silane coupling agent, all as described in Example 2. Using the resin formulations of Example 1, it was found that only 317 g of the filler material of this example could be incorporated into the resin (as compared to 525 grams of filler in Example 3). Attempts to incorporate additional filler resulted in a dry mixture unsuitable for use as a dental restorative material.

Test specimens were made according to the standards of the American Dental Association Specification No. 9 for compressive strength. After storage for 24 hours at 37°C., the test samples are crushed yielding a compressive strength of 45,000 p.s.i. This polymerized dental restorative composition gave a Barcol Hardness value of 80 after 24 hours storage in distilled water at 37°C.

This example demonstrates that a narrow particle size distribution for the particulate filler inherently limits the amount of filler which may be incorporated into the dental restorative material (with accordingly lower compressive strength).

WHAT WE CLAIM IS:—

1. A composite dental restorative material prepared by mixing and polymerizing a liquid organic polymerizable binder and a finely divided particulate filler, the filler having a particle size distribution such that 70 to 95% by weight of said particles are in the range of 0.7 to 25 microns and correspondingly 5 to 30% by weight of said particles are in the range of 0.2 to 0.7 micron.

2. A composite dental restorative material in accordance with claim 1, wherein 75 to 85% by weight of said particles are in the

range of 0.7 to 20 microns and correspondingly 15 to 25% by weight of said particles are in the range of 0.2 to 0.7 micron.

5 3. A composite dental restorative material in accordance with claim 1 or claim 2 wherein said particles are alpha quartz.

10 4. A composite dental restorative material in accordance with any preceding claims wherein said particulate filler comprises about 75 to 90% by weight of said restorative material.

15 5. A composite dental restorative material in accordance with any preceding claim wherein said polymerizable binder comprises the glycidyl methacrylate derivative of Bisphenol A.

20 6. A composite dental restorative material in accordance with any preceding claim wherein said binder further contains a reactive diluent.

25 7. In a method for filling a cavity in a tooth, which method comprises the steps of filling said cavity with a blend of liquid polymerizable organic binder and a finely divided particulate filler, and thereafter hardening said blend in situ, the filler having a particle size distribution such that 70 to 95% of said particles are in the range of 0.7 to 25 microns and correspondingly 5 to 30% by weight of said particles are in the range of 0.2 to 0.7 micron.

8. A method in accordance with claim 7, wherein 75 to 85% by weight of said particles are in the range of 0.7 to 20 microns and correspondingly 15 to 25% by weight of said particles are in the range of 0.2 to 0.7 micron, and wherein said particulate filler comprises about 75 to 90% by weight of said restorative material.

9. A method in accordance with claim 7 or claim 8 wherein said particles are alpha quartz.

10. A method in accordance with any of claims 7 to 9 wherein said polymerizable binder comprises the glycidyl methacrylate derivative of Bisphenol A and a reactive diluent.

11. Composite dental restorative material according to Claim 1 and substantially as herein described with reference to the Examples.

12. A method of filling a cavity in a tooth according to Claim 7 and substantially as herein described.

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